

MODIFIED CLAIMS (Article 34, PCT)

1. Process for the preparation of a low-viscosity (poly)isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp^3 carbon atoms, characterized in that the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of at least 50°C and of not more than 200°C for a period of not more than 24 hours.
2. Process according to Claim 1, characterized in that the starting reaction medium is heated to a temperature of at least 80°C, preferably of at least 120°C, and of not more than 170°C.
3. Process according to Claim 1 or 2, characterized in that the reaction medium is heated along a decreasing temperature gradient.
4. Process according to any one of the preceding claims, characterized in that the heating time is at least 5 minutes, preferably at least 30 minutes, and not more than 24 hours, preferably not more than 5 hours.
5. Process according to any one of the preceding claims, characterized in that at the end of the dimerization reaction, the starting monomer is removed, in particular by distillation.
6. Process according to any one of Claims 1 to 4 for the continuous preparation of a composition containing at least one isocyanate dimer containing a uretidinedione unit, characterized in that after the dimerization reaction, the unreacted monomers are removed and are recycled into the dimerization step.
7. Process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers, in which the isocyanate groups are borne by sp^3 carbon atoms,

and optionally from other monomers, this process comprising the following steps:

- i) the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of at least 80°C, preferably of at least 120°C, and of not more than 200°C, advantageously of not more than 170°C, for a period of less than 24 hours, advantageously of less than 5 hours;
 - ii) the reaction product from step i) containing unreacted monomers is reacted with a (cyclo)condensation catalyst, under (cyclo)trimerization conditions;
 - iii) the unreacted starting monomers are removed from the reaction product from step ii);
 - iv) the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer is isolated.
8. Process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp^3 carbon atoms, and optionally from other monomers, this process comprising the following steps:
- i) the starting monomers are reacted with a (cyclo)trimerization or (cyclo) condensation catalyst under (cyclo)trimerization or (cyclo)condensation conditions;
 - ii) the reaction product from step i) containing unreacted isocyanate monomers is heated, in the absence of dimerization catalyst, to a temperature of at least 80°C, preferably of at least 120°C, and of not more than 200°C, advantageously of not more than 170°C, for a period of less than 24 hours, advantageously of less than 5 hours;
 - iii) the unreacted starting monomers are removed from the reaction product from step ii);
 - iv) the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer is isolated.

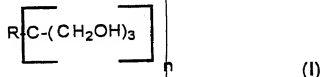
5. Process for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound having a function derived from the isocyanate function, starting with isocyanate monomers in which the isocyanate groups are borne by sp^3 carbon atoms and another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:
- 10 i) the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of greater than at least 80°C , advantageously at least 120°C , preferably at least 130°C , and less than at least 200°C , advantageously at least 170°C , for a period of less than 24
 - 15 hours, advantageously less than 5 hours;
 - ii) the reaction product from step i) containing unreacted isocyanate monomers and a compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are reacted
 - 20 together, optionally in the presence of a catalyst;
 - iii) the isocyanate monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are removed from the reaction
 - 25 product from step ii);
 - iv) the polyfunctional isocyanate composition of low-viscosity comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other function derived from the isocyanate function, is isolated.
- 30 16. Process for the preparation of a low-viscosity polyisocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound containing a function derived from the isocyanate function, starting with isocyanate monomers
- 35 in which the isocyanate groups are borne by sp^3 carbon atoms and with another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following

steps:

- i) an isocyanate monomer is reacted with a compound comprising at least one function other than an isocyanate function, which is reactive with the isocyanate function, optionally in the presence of a catalyst;
- ii) the reaction mixture from step i) containing unreacted isocyanate monomers is heated, in the absence of dimerization catalyst, to a temperature of greater than at least 80°C, advantageously at least 120°C, preferably at least 130°C and not more than 200°C, advantageously not more than 170°C, for a period of less than 24 hours, advantageously less than 5 hours;
- iii) the monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are removed from the reaction product from step ii);
- iv) the low-viscosity polyisocyanate composition comprising at least one polyisocyanate trimer and at least one polyisocyanate dimer is isolated.
- 11.Process according to any one of Claims 7 to 10, characterized in that the isocyanate dimer is obtained by heating the reaction medium along a decreasing temperature gradient.
- 12.Process according to Claim 9 or 10, characterized in that the function derived from the isocyanate function is a carbamate, allophanate, urea, biuret and/or masked isocyanate function.
- 13.Process according to Claim 9 for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function, comprising the reaction, in step ii), of isocyanate monomers with water.
- 14.Process according to Claim 10 for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function,

comprising the reaction, in step i), of isocyanate monomers with water.

15. Process according to any one of the preceding claims, characterized in that, for the dimerization of the starting
5 monomers, a compound of general formula I:

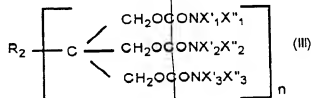
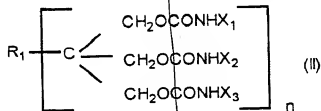


in which

- R is a mono- or n-valent hydrocarbon-based group having from 1 to 30 carbon atoms, in which the hydrocarbon-based
10 chain can be interrupted by one or more chalcogen atoms and can bear 1 to 3 OH groups, and n is an integer ranging from 1 to 3,

- and/or products derived from this derivative by a reaction with a compound bearing an aliphatic isocyanate function,
15 is added to the reaction medium containing the starting monomers.

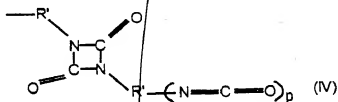
16. Process according to Claim 15, characterized in that the said products derived from the reaction of the compound of general formula I with a compound bearing an aliphatic
20 isocyanate function correspond to the general formulae II and/or III below:



- 25 in which

one or more of X_1 , X_2 and X_3 represents a group $\text{R}'-(\text{N}=\text{C}=\text{O})_p$,

in which R' is a p-valent aliphatic group and p is an integer ranging from 0 to 5, the others representing, where appropriate, a group of formula



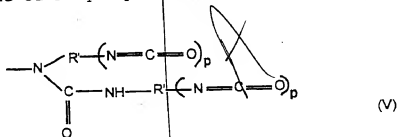
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R' and p being as defined above,

R₁ is R, with the OH groups substituted, where appropriate, with a group CONX₁H, X₁ being as defined above,

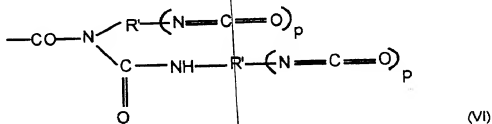
at least one of NX'₁X''₁, NX'₂X''₂, and NX'₃X''₃, represents the

10 group



R' and p being as defined above, the others representing a group NX₁H or NX₁-silyl with X₁ as defined above and

R₂ being R, with the OH groups substituted, where

15 appropriate, with a group CONX₁H, or

R' and p being as defined above, and

n is an integer ranging from 1 to 3.

17.Process according to Claim 15 or Claim 16, characterized in that R is a C₁-C₄ alkyl group substituted with 1 to 3 OH

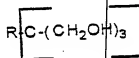
20 groups.

18.Process according to any one of Claims 15 to 17, characterized in that the compound of general formula I is selected from pentaerythritol and trimethylolpropane, and the compounds of general formulae II and III are selected,

where appropriate, from the corresponding pentaerythritol and trimethylolpropane derivatives as defined in Claim 16.

19. Process according to any one of the preceding Claims, characterized in that the starting isocyanate monomers are
- 5 diisocyanates selected from hexamethylene diisocyanate, tetramethylene diisocyanate, norbornane dimethylene diisocyanate, isophorone diisocyanate, bis(isocyanato)cyclohexylmethane and 2-methylpentamethylene diisocyanate.

20. Use of a compound of general formula I:



(I)

- 15 in which

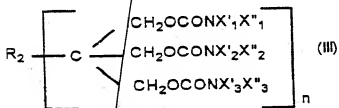
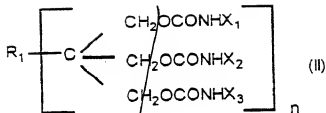
R is a mono- or n-valent hydrocarbon-based group having from 1 to 30 carbon atoms, in which the hydrocarbon-based chain can be interrupted by one or more chalcogen atoms and can bear 1 to 3 OH groups, and n is an integer

- 20 ranging from 1 to 3,

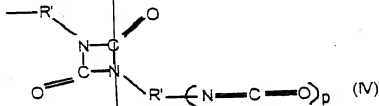
and/or products derived from this derivative by reaction with a compound bearing an aliphatic isocyanate function, for the preparation of isocyanate dimers from aliphatic isocyanate monomers, with a degree of conversion of at

25 least 5%, preferably at least 10%, of the starting isocyanate functions into uretidinedione functions.

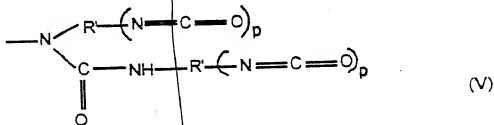
21. Use according to Claim 20, characterized in that the said products derived from the reaction of the compound of general formula I with a compound bearing an
- 30 aliphatic isocyanate function correspond to the general formulae II and/or III below:



in which
 one or more of X_1 , X_2 and X_3 represents a group $R'-(N=C=O)$,
 in which R' is a p-valent aliphatic group and p is an
 integer ranging from 0 to 5,
 5 the others representing, where appropriate, a group of
 formula

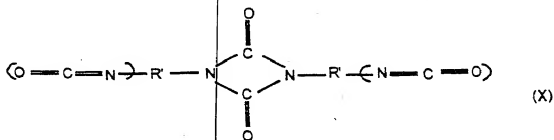


R' and p being as defined above,
 R_1 is R, with the OH groups substituted, where
 appropriate, with a group CONX_1H , X_1 being as defined
 10 above,
 at least one of $\text{NX}'_1\text{X}''_1$, $\text{NX}'_2\text{X}''_2$, and $\text{NX}'_3\text{X}''_3$, represents
 the group



$$\begin{array}{c} \text{---CO---N---R---(N---C---O)}_p \\ | \\ \text{C---NH---R'---(N---C---O)}_p \\ || \\ \text{O} \end{array}$$

5 R' and p being as defined above, and
n is an integer ranging from 1 to 3,
for the preparation of dimeric compounds of general
formula X:



in which R' and p are as defined in Claim 20, starting
10 with isocyanate monomers of general formula VII:



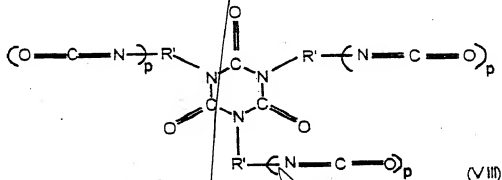
R' and p being as defined above, with a degree of conversion of advantageously 5%, preferably 10% at least of the isocyanate functions into compounds of formula X.

15 22. Use according to Claim 20 or Claim 21, character-
ized in that R is a C-C₄ alkyl group substituted with 1
to 3 OH groups.

23. Use according to Claim 21, characterized in that the compound of general formula I is selected from pentaerythritol and trimethylolpropane, and the compounds of

general formulae II and III are selected, where appropriate, from the corresponding pentaerythritol and trimethylolpropane derivatives as defined in Claim 21.

24. Use according to Claim 21, characterized in that
 5 the reaction for the preparation of the compounds of general formula X from the compounds of general formula VII is carried out in a reaction medium also comprising compounds of general formula VIII:

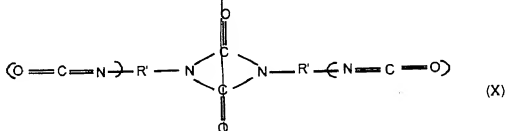


in which R' and p are as defined in Claim 21.

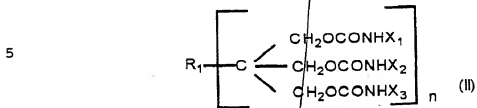
- 10 25. Use according to Claim 21, characterized in that the compound of general formula I, and/or III and/or III is bound to a support, in particular a resin.

26. Low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer
 25 and at least one compound having a biuret function, characterized in that the biuret unit containing compound represents at least 10%, advantageously at least 10 %, preferably at least 20%, by weight.

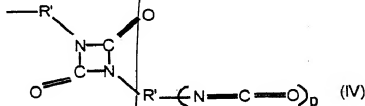
27. Composition comprising at least one compound of
 30 general formula X :



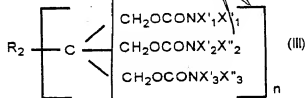
in which R' and p are as defined in Claim 21,
and at least one compound of general formula II:



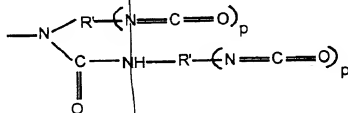
10 in which one or more of X₁, X₂ and X₃ represents a group
-R'-N=C=O as defined above and the others represent,
where appropriate, a group



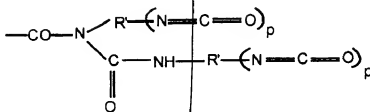
R' and p being as defined above,
and R₁ is R, with the OH groups substituted, where
appropriate, with a group CONX₁H as defined above,
15 and n being an integer from 1 to 3,
and/or at least one compound of general formula III:



in which at least one of NX'₁X''₁, NX'₂X''₂ and NX'₃X''₃,
represents the group

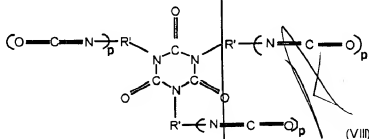


R' and p being as defined above, the others representing
20 a group NX₁H with X₁ as defined above, and



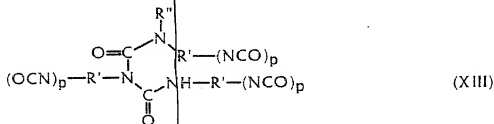
and n is an integer ranging from 1 to 3,

- 5 and/or a biuret compound obtained from an isocyanate of
general formula VI as define in claim 21, the said
composition also being characterized in that it is free
of dimerization catalyst of phosphine, aminopyridine,
phosphoramidate, organometallic or tertiary amine type.
- 10 28. Composition according to Claim 27, characterized in
that it also comprises a compound of general formula
VIII:



R' and p are as defined above,

- 15 and/or a compound of general formula XIII :



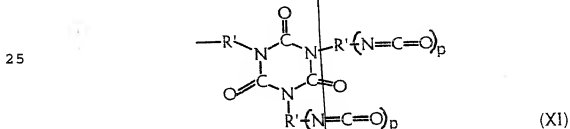
wherein R" represents H or a hydrocarbon group and R' and p are as defined above.

29. Composition comprising at least one compound of general formula X as defined in Claim 27 and/or optionally one compound of general formula VIII as defined in Claim 28 and/or at least one compound of general formula XIII as defined in claim 24, the said composition being free of dimerization catalysts.

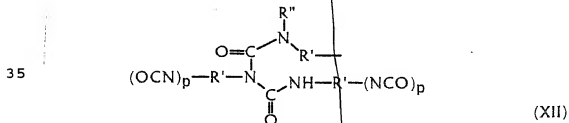
30. Compound of general formula III as defined in claim 16, in which at least one of the groups $NX'_1X''_1$, $NX'_2X''_2$, and $NX'_3X''_3$, represents the group of formula V as defined above, the others representing a group NX_iH with X_1 , $X'_1X''_1$, $X'_2X''_2$, and $X'_3X''_3$, as defined in claim 16 and R^1 as defined in Claim 16, i.e. representing a group R with the OH groups substituted, where appropriate, with a group CO- NX_iH or a group of formula V, as defined in Claim 16.

31. Compound of formula III in which :

- the groups $NX'_1X''_1$, $NX'_2X''_2$, and $NX'_3X''_3$, are selected from a group of general formula NX_iH , a group of general formula V as defined above, a uretidinedione group of formula IV, an isocyanurate group of formula XI :



30 R' and p being as defined in Claim 16, a biuret group of formula XII :



R' and p being as defined in Claim 16,

- R" represents H or a hydrocarbon-based group,
 R₂ represents the group R with the OH groups substituted,
 where appropriate, with a group selected from CONHX₁, a
 group of formula VI, a group of formula VI, a group of
 5 formula -CO-NH- (group of formula IV), -CO-NH- (group of
 formula XI) and -CO-NH- (group of formula XII), with the
 proviso that the compounds containing at least one
 carbamate group of formula NX₂H, or CONHX₂H respectively,
 and/or allophanate group of formula V, or -CO-NH- (group
 10 of formula V) respectively, and at least one group
 selected from a uretidinedione group of general formula
 IV, or -CO-NH- (group of general formula IV),
 respectively, an isocyanurate group of general formula
 XI, or -CO-NH- (group of general formula XI)
 15 respectively, and a biuret group of general formula XII,
 or -CO-NH- (group of general formula XII) respectively.
32. Compounds according to Claim 30 or Claim 31, in
 which p is equal to 1 and containing 1, 2, 3 or 4
 allophanate groups.
- 20 33. Compounds according to Claim 30 or Claim 31,
 characterized in that R' is a group selected from a
 group (CH₂)_n with n ranging from 2 to 8, optionally
 substituted with a hydrocarbon-based chain optionally
 bearing an isocyanate function, a norbornylmethylene
 25 group, a cyclohexylmethylene group or a 3,3,5-
 trimethylcyclohexyl methylene group.
34. Use of a composition according to Claim 27 or Claim
 28 for the preparation of a polyurethane coating.
35. Composition for simultaneous or successive
 30 application, comprising :
 - at least one polyisocyanate composition according
 to one of Claims 26 to 29 ; and
 -a polyol.
36. Composition according to Claim 35, characterized in
 35 that the polyol is a polyol of acrylate type which
 satisfies the following conditions for a dry extract
 (DE) of 75-80 % by weight :
 - Mw (weight-average molecular weight) not greater
 than 10,000, advantageously not greater than 5000,

preferably not greater than 2000 ;

- Mn (number-average molecular weight) of not greater than 5000, advantageously not greater than 3000, preferably no greater than 800 ;

5 - Mw/Mn (dispersity ratio) of not greater than 5, advantageously not greater than 3, preferably not greater than 2 ;

- number of OHs/molecule of greater than or equal to 2, advantageously greater than 2.

10 37. Composition according to Claim 35, characterized in that the polyol is a polyol of polyester type having 100 % dry extract and a viscosity of not greater than 10,000 mPa.s, advantageously not greater than 5000 mPa.s, preferably not greater than 1000 mPa.s, and an Mw of
15 between 250 and 8000.

38. Composition according to one of Claims 35 to 37, containing a crosslinking catalyst, which is optionally a latent catalyst.

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